

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
13 September 2001 (13.09.2001)

PCT

(10) International Publication Number  
**WO 01/67465 A2**

(51) International Patent Classification<sup>7</sup>: **H01B 3/00**

North York, Ontario M2P 1B1 (CA). **FARRELL, Mark**;  
RR#4, P.O. Box 687, Georgetown, Ontario L9Y 4E8 (CA).

(21) International Application Number: PCT/IB01/00290

(22) International Filing Date: 1 March 2001 (01.03.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/518,532 4 March 2000 (04.03.2000) US

(71) Applicant: **ENERGENIUS, INC.** [CA/CA]; 840 York  
Mills Road, North York, Ontario M3B 3A8 (CA).

(72) Inventors: **ZOU, Qin**; 260 Wellesley Street East, Apt.  
2218, Toronto, Ontario M4X 1G6 (CA). **YACOBI, Ben**,  
G.; 1700 The Collegeway, #405, Mississauga, Ontario L5L  
4M2 (CA). **RUDA, Harry, Eugen**; 21 Brookfield Road,

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,  
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,  
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,  
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,  
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,  
TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

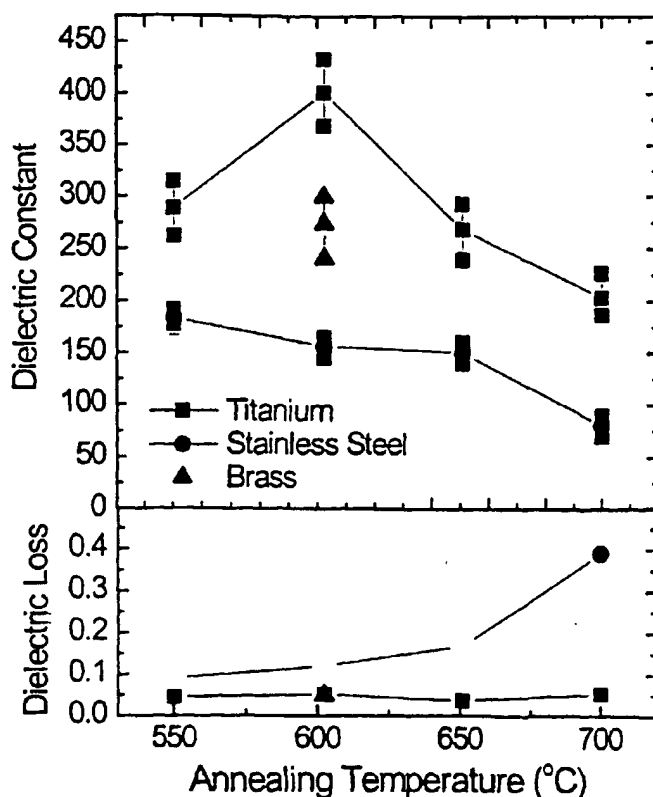
(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished  
upon receipt of that report

[Continued on next page]

(54) Title: LEAD ZIRCONATE TITANATE DIELECTRIC THIN FILM COMPOSITES ON METALLIC FOILS



(57) Abstract: Crystalline dielectric lead zirconate titanate thin film composites on metallic foils exhibit high dielectric constants, low dielectric loss (loss tangent of less than 5 %) and low leakage current. The lead zirconate titanates may be of the formula  $PbZr_xTi_yO_z$  (PZT) herein x and y are independently from about 0.35 to about 0.65 and z is from about 2.5 to about 5.0. The thin foil dielectric composites can be prepared by a variety of methods including deposition of PZT thin films on brass, platinum, titanium and stainless steel foils using sol-gel processing, sputtering deposition and chemical vapor deposition.

WO 01/67465 A2



---

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**APPLICATION FOR PATENT**

**TITLE:                   LEAD ZIRCONATE TITANATE DIELECTRIC THIN FILM  
COMPOSITES ON METALLIC FOILS**

**SPECIFICATION****Field of the Invention**

The invention relates to crystalline dielectric thin film structures on metallic foils. Such thin foil dielectric systems can be prepared, for example, by depositing  $\text{PbZr}_x\text{Ti}_y\text{O}_z$  (PZT) thin films on selected metallic substrates such as brass, platinum, titanium and stainless steel foils using sol-gel methods, sputtering deposition methods, or metal-organic chemical vapor deposition.

**Background of the Invention**

Lead zirconate titanate (PZT) thin films have attracted considerable interest as potential candidate materials for electronic and optoelectronic applications, such as ferroelectric memory devices, pyroelectric sensor devices, waveguide modulators and acoustic sensors. Most PZT films are currently deposited on silicon substrate with a Pt bottom electrode limiting their range of potential applications. Alternative structures are desired which permit high frequency operation range, low dielectric loss, low ESR, and the potential for embedded capacitor systems.

Previous attempts at depositing dielectric films on metal substrates have been reported in the literature. For example, Saegusa (*Japanese Journal of Applied Physics*, Part 1, vol. 36, no. 11; Nov. 1997; p. 6888-93) reported on the deposition of non-crystalline (glassy) films of  $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  (PZT) thin films on aluminum, titanium and stainless steel foils. The resulting products, however, do not exhibit the requisite properties needed for commercial applications.

### **Summary of the Invention**

The invention relates to crystalline dielectric thin film structures on metallic foils. Such thin foil dielectric systems can be prepared, for example, by depositing  $\text{PbZr}_x\text{Ti}_y\text{O}_2$  (PZT) thin films on brass, platinum, nickel alloys, titanium and stainless steel foils using various methods such as sol-gel processing, sputtering deposition, and metal-organic chemical vapor deposition. The crystalline dielectric films of the invention include single-crystalline, poly-crystalline, and nano-crystalline films, i.e., films with grain sizes varying from nanometer-scale to cm-scale.

The crystalline dielectric thin film structures of the invention exhibit excellent properties for capacitors, including high dielectric constant ( $\epsilon=400$ ), low dielectric loss (loss tangent of  $<5\%$ ) and low leakage current (below  $5 \times 10^{-7}$  A at 5V). In addition, the thin film structures of the invention exhibit high frequencies.

### **Brief Description of the Drawings**

FIG. 1 is a schematic drawing of various configurations for crystalline dielectric thin film structures on metallic foils.

FIG. 1(a) is a structure composed of a crystalline dielectric thin film deposited on a metallic foil.

FIG. 1(b) is a structure composed of a crystalline dielectric thin film deposited on a metallic foil that also includes an interposed barrier layer between the dielectric film and a metallic foil.

FIG. 1(c) is a structure composed of a single or multiple different crystalline dielectric thin films deposited on a metallic foil that also includes various interposed barrier layers between the dielectric film and a metallic foil.

FIG. 1(d) is a structure composed of a single or multiple different crystalline dielectric thin films deposited on a metallic foil that also includes an interposed buffer layer in addition to various barrier layers interposed between the dielectric film and metallic foil.

FIG. 1(e) represents an embodiment offering an enhanced surface area wherein a textured substrate is employed incorporating the various combinations as described for FIGS. 1(a) to 1(d).

FIG. 1(f) represents an embodiment offering an enhanced surface area wherein a porous structured substrate is employed incorporating the various combinations as described for FIGS. 1(a) to 1(d).

FIG. 1(g) represents an embodiment of a parallel interconnection of many dielectric metallic foil systems.

FIG. 1(h) represents an embodiment of a series interconnection of many dielectric metallic foil systems.

FIG. 2 is a plot of the dielectric constant of PZT films formed on selected metallic foils as a function of annealing temperature for selected metallic foils. The thickness of the film is about 660 nm, the electrode area is  $0.5 \text{ mm}^2$  and the dielectric constant was measured at 10 kHz at room temperature.

FIG. 3 is a plot of the dielectric constant as a function of frequency for selected metallic foils, i.e., titanium (sample T600), stainless steel (S550), and brass (B600). Films were as depicted above and measured at room temperature at zero bias with modulation voltage of 200 mV.

FIG. 4 represents current voltage curves for PZT films on different metal substrates. Inset shows  $I-V^{1/2}$  curves. The thickness of the film is about 660 nm, the electrode area is  $0.5 \text{ mm}^2$  with measurements made at room temperature.

FIGS. 5(a)-5(c) represent plots of dielectric constants as a function of electric field for the PZT films on stainless steel (FIG. 5(a)), titanium (FIG. 5(b)), and brass (FIG. 5(c)) substrates, measured at room temperature and a frequency of 10 kHz frequency.

#### Detailed Description of the Preferred Embodiment

A crystalline dielectric thin film composite contains a metallic foil as substrate. The metal of the foil should possess a high melting point, exhibit a close match of thermal expansion coefficient to PZT, show low reactivity with PZT, and permit good

adhesion with PZT. The melting point is most preferably at least 850°C. Preferably, the thin film composite incorporates one or more barrier layers, various buffer layers, along with a dielectric thin-film. In a preferred embodiment, the dielectric material is of the formula  $\text{PbZr}_x\text{Ti}_y\text{O}_z$  wherein both x and y are about 0.5 and z is about 2.5 to about 5.

5       The inorganic oxides forming the dielectric are bonded to the substrate. Such oxides exhibit a tetragonal or perovskite crystalline lattice. The inorganic oxides may further exhibit dielectric, ferroelectric and/or paraelectric properties.

      In a preferred embodiment, the laminate is one wherein the inorganic oxides are interposed between two substrate layers; the substrates being independently selected from  
10 different types of electrically conductive metals or from different types of non-conducting and electrically conductive substrates having a melting point of at least 850°C.

      In general, the oxide films as-deposited are only partially crystalline. Since the dielectric properties are enhanced by film crystallinity, a post deposition thermal  
15 treatment is often used. This can be accomplished by rapid thermal annealing using quartz halogen lamps, laser-assisted annealing (such as that wherein an excimer or carbon dioxide laser is employed) or an electron beam annealing.

      The thin films or plates of the invention may be made by a sol-gel process. This process is preferred since it renders film composites of high purity. In addition, the sol-gel process employs low processing temperatures. Crystallization temperatures are  
20 normally between 500 and 700°C. Deposition of PZT on a metallic substrate requires a low processing temperature to minimize interdiffusion and reaction between the foil and the dielectric. Further, the composition is easily controlled by use of the sol-gel process.

      The dielectric material for use in the invention may contain a metal of the  
25 lanthanide series. Preferably either La or Nb is used. Suitable dielectrics include those of the formula  $\text{Pb}_a\text{L}_b\text{Zr}_x\text{Ti}_y\text{O}_z$  wherein L is a lanthanide metal, preferably La or Nb, x and y are independently between from about 0.35 to about 0.65, z is from about 2.5 to about 5.0, a is from about 0.95 to about 1.25 and b is from about 0.02 to about 0.10. Such dielectrics may be prepared by using, as starting materials, lead acetate

[ $\text{Pb}(\text{CH}_3\text{COO})_2\text{H}_2\text{O}$ ], zirconium n-propoxide [ $\text{Zr}(\text{O}-\text{nC}_3\text{H}_7)_4$ ], titanium isopropoxide [ $\text{Ti}(\text{O}-\text{iC}_3\text{H}_7)_4$ ] and lanthanum isopropoxide [ $\text{La}(\text{O}-\text{iC}_3\text{H}_7)_3$ ] or niobium ethoxide [ $\text{Nb}(\text{OC}_2\text{H}_5)_5$ ]. In a preferred method, the dielectric is prepared by dissolving lead acetate trihydrate in 2-methoxyethanol and dehydrating the composition at 110°C under vacuum to obtain lead acetate. Zirconium n-propoxide and titanium isopropoxide in 2-methoxyethanol may then be admixed with the resulting product which is at room temperature, then refluxed at 110°C for about 2 to 3 hours under vacuum from which polymer precursors, such as those of the formula  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ , may be obtained. Finally, the 0.3 M stock solutions may be obtained by dilution with toluene and adding appropriate formamide for protecting from crack and 10 mol% excess Pb for loss of lead oxide during the final annealing processing.

The PZT solution is deposited using spin-coating technology on various metal foils, such as titanium foil (thickness, d, is 0.054 mm, surface roughness, Ra, is 550 nm); aluminum foil (d=0.05 mm, Ra=200 nm); stainless steel foil (d=0.052 mm, Ra=540 nm); brass sheet (d=1.2 mm, Ra=60 nm); or nickel alloy sheet (d=1.5 mm, Ra≈800 nm). Before deposition the substrates are cleaned, such as by using acetone (in an ultrasonic cleaner), to remove oil. The spin speed used is typically 2000 rpm for 30 s. Each spin on the layer is then dried at 200°C for 5~10 min on the hot plate. The thickness of each layer is about 110 nm. The deposited films may then be fired at 450°C for 20 min and then crystallized at 600°C for 30 min using rapid thermal annealing (RTA).

The dielectric constant of the thin film composites of the invention may be more than 400. To obtain the desired high values of dielectric constant for the thin films, a ferroelectric, dielectric and/or paraelectric phase transition is induced. The onset of this transition depends on the annealing temperature. Thus, the product is annealed at elevated temperature until crystallization. Generally, the annealing temperature is between from about 600°C to about 800°C. Higher annealing temperatures tend to increase the average grain sizes in the films.



## Examples

### **Example 1.**

#### ***PZT precursor preparation.***

The starting materials for PZT film preparation was lead acetate  
5 [Pb(CH<sub>3</sub>COO)<sub>2</sub>H<sub>2</sub>O], zirconium n-propoxide [Zr(O-nC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>], titanium isopropoxide  
[Ti(O-iC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>] and lanthanum isopropoxide [La(O-iC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>] or niobium ethoxide  
[Nb(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub>].

PZT stock solution was prepared basically by dissolving lead acetate trihydrate in  
2-methoxyethanol and dehydrating it at 110°C under vacuum to obtain Pb acetate. The  
10 zirconium n-propoxide and titanium isopropoxide in 2-methoxyethanol was then mixed at  
room temperature. The Zr+Ti solution was added to the Pb acetate which was then  
refluxed at 110°C for two to three hours under vacuum ambient and finally distilled by  
product. A Pb(Zr<sub>0.52</sub>Ti<sub>0.48</sub>)O<sub>3</sub> polymer precursor was obtained. Finally, a 0.3 M stock  
solution was obtained by dilution with toluene and adding appropriate formamide for  
15 protecting from crack and 10 mol% excess Pb for loss of lead oxide during the final  
annealing processing.

#### ***Deposition.***

A PZT precursor solution was then deposited using spin-coating technology onto:

Titanium foil (thickness(d)=0.054 mm, surface roughness(Ra=550 nm);

20 Aluminum foil (d=0.05 mm, Ra=200 nm);

Stainless steel foil (d=0.052, Ra=540 nm);

Brass sheet (d=1.2 mm, Ra=60 nm);

Nickel alloy sheet (d=1.5 mm, Ra≈800 nm).

Before deposition, the substrates are preferably cleaned using acetone under  
25 ultrasonic to remove oil. The spin speed was 2000 rpm for 30 seconds. Each spin on the  
layer was dried at 200°C for 5~10 min on the hot plate. The thickness of each layer was  
about 110 nm.

***Heat treatment.***

The deposited films were then fired at 450°C for 20 min and then crystallized at 600°C for 30 min using rapid thermal annealing (RTA).

- It is most preferably that all reactants used in the process be of high purity. Generally, the level of purity is greater than 90%, preferably greater than 95%, most preferably greater than 99%. In addition, it is preferred that the individual steps of the invention be conducted in a nitrogen-free atmosphere.

The samples obtained and tested are tabulated in Table 1.

TABLE 1

Sample Code	Ti550	Ti600	Ti650	BR600	SS550	SS600	SS650
Substrate	Titanium			Brass	Stainless Steel		
Film precursor	PZT Polymer in Toluene (as described in Experimental Sect.)						
Annealing Temperature (°C)	550	600	650	600	550	600	650
Dielectric constant	288	480	256	305	192	165	150
Thickness of PZT (nm)	660						

10

The thin film composites were measured at room temperature at zero bias with modulation voltage of 200 mV. Figure 2 demonstrates the effect of annealing temperature on the dielectric constant of PZT films deposited on selected metallic foil substrates.

**Example 2.**

- 15 PZT precursors were prepared as set forth in Example 1. 650-nm thick PZT films were then spin-coated onto a variety of metallic foils including (a) titanium foil (thickness  $d=0.4$  mm, surface roughness,  $R_u=550$  nm), aluminum foil ( $d=0.05$  mm,  $R_u=300$  nm), stainless steel foil (SS) ( $d=0.042$ ,  $R_u=400$  nm), brass sheet (BR) ( $d=1.2$  mm,  $R_u=60$  nm) and nickel alloy sheet (NK) ( $d=1.5$  mm,  $R_u\approx 800$  nm). Evaporated Au  
20 top electrodes with an area of  $5\times 10^{-3}$  cm<sup>2</sup> were used to measure dielectric properties. The

capacitance-voltage (C-V), capacitance-frequency (C-f) and current-voltage (I-V) measurements were performed using a HP 4275A LCR meter and a HP 4140B picoammeter at room temperature. The hysteresis behavior was examined using a Radiant RT6000S ferroelectric test system.

- 5 Table 2 summarizes the results of the room temperature dielectric property measurements on the selected substrates:

TABLE 2

Substrate	Sample code	Annealing temp. (°C)	Dielectric constant (10 kHz)	Dielectric loss (%) (10 kHz)	Breakdown voltage (KV/cm)	DC resistance at 1V (GΩ)
Titanium	Ti600	600	400	4.0	600	5000
Stainless steel	SS650	650	155	15	590	0.25
Brass	BR600	600	256	4.8	288	0.13
Nickel alloy	NK600	600	20	2.1		7000

10

X-ray photoelectron spectroscopy (XPS) showed that the PZT film on Ti foil had a Ti/TiO<sub>x</sub>/PZT structure. This is likely due to the formation of a titania (TiO<sub>x</sub>) layer with relatively low dielectric constant ( $\epsilon < 80$ ) between the Ti and PZT.

- FIG. 3 shows the dielectric constant and loss as a function of frequency. These capacitor systems have excellent frequency characteristics, with the dielectric constant remaining virtually constant up to 1 MHz. These types of capacitors can potentially be used in high frequency applications.

- Figure 2 shows the dielectric constant and loss as a function of PZT annealing temperature. For PZT/Ti foil, an optimum annealing temperature was about 600°C, at which the higher dielectric constant and low loss were obtained. Above this temperature, dielectric constant decreased with increasing annealing temperature. This may be attributed to increased thickness of the titania with annealing temperature. Where the foil

was stainless steel, the dielectric constant decreased, but the dielectric loss greatly increased with increasing annealing temperature in the range of 550-700°C. This reflects the increased concentration of Cr and Ni diffusing into the PZT film. The higher annealing temperature likely results in much deeper diffusion of Ni and Cr.

5        FIG. 3 shows the current-voltage curves for the stainless steel (SS600) and brass (BR600) based capacitors. The titanium (Ti650) and stainless steel (SS600) capacitors showed the lowest leakage current,  $10^{-12}$  A to  $10^{-8}$  A, up to 5V. In the insert to Fig. 3, this data is presented in a standard Schottky plot, with all the data following  $\log(I/T^2) = AV^{1/2}$ , where I is the current, T is the temperature, V is the applied voltage, and A is a constant.  
10    For the case of the Ti650 capacitor, there are two different slopes. This behavior again probably reflects the titania layer between the PZT and Ti foil.

FIGS. 5(a) through 5(c) shows the dielectric constant as a function of electric field for various metal substrates at 10 kHz. The  $\epsilon$ -E characteristics on titanium (FIG. 5(b)), stainless steel (Fig. 5(a)), and brass (Fig. 5(c)), metal substrates are quite different. For  
15    PZT on stainless steel, the C-V behavior is that of a typical ferroelectric material. The maximum dielectric constant of about 150 was obtained for a coercive field of 25 kV/cm. The data for the brass substrate implies that at the interface between PZT and brass, a semiconducting layer was formed after high temperature annealing.

The examples show the fabrication of ferroelectric PZT films on titanium,  
20    stainless steel, brass, and nickel alloy substrates, using sol-gel processing and annealing. The PZT films on these substrates were crack-free, and showed strong adhesion without any signs of delamination. Capacitor with relatively high dielectric constant ( $\epsilon \approx 400$ ), low dielectric loss ( $\tan \delta < 5\%$ ), low leakage current ( $I_L < 5 \times 10^{-8}$  A at 5V) and high breakdown field strength were obtained. Excellent high frequency properties were observed in the  
25    case of capacitors on titanium, stainless steel, and brass substrates.

Various modifications may be made in the native, composition, operation, and arrangement of the various elements, steps and procedures described herein without departing from the spirit and scope of the invention as defined in the following claims.

CLAIMS

What is claimed is:

- 1 1. A multi-layer thin film composite comprising a metallic foil substrate and at least  
2 one crystalline dielectric layer.
- 2 2. The thin film composite of Claim 1, wherein the metallic foil is an elemental  
metal.
- 1 3. The thin film composite of Claim 2, wherein the metallic foil is either a flat  
2 surface, textured surface or macroporous surface.
- 1 4. The thin film composite of Claim 1, wherein the dielectric layer is composed of a  
2 single layer of a dielectric material.
- 1 5. The thin film composite of Claim 1, wherein the dielectric layer is composed of  
2 multiple layers of dielectric materials in a regular or irregular superlattice structure.
- 1 6. The thin film composite of any of Claims 1-5, wherein a barrier layer is  
2 interposed between the metallic substrate and the dielectric material.

- 1 7. The thin film composite of Claim 1, wherein the dielectric is  $\text{PbZr}_x\text{Ti}_y\text{O}_z$  wherein  
2 x and y are independently between from about 0.35 to about 0.65 and z is between from  
3 about 2.5 to about 5.0.
- 1 8. The thin film composite of Claim 7, wherein x and y are 0.5 and z is 3.
- 1 9. The thin film composite of Claim 7, wherein x is 0.48, y is 0.52, and z is 3.
- 1 10. The thin film composite of Claim 7, wherein the thin film or plate has a dielectric  
2 constant of at least 400.
- 1 11. The thin film composite of Claim 7, wherein the thin film or plate has a dielectric  
2 thickness between from about 100 to about 1000 nm.
- 1 12. The thin film composite of Claim 1, wherein the dielectric is  $\text{Pb}_a\text{La}_b\text{Zr}_x\text{Ti}_y\text{O}_z$  or  
2  $\text{Pb}_a\text{Nb}_b\text{Zr}_x\text{Ti}_y\text{O}_z$  wherein x and y are independently between from about 0.35 to about  
3 0.65, z is from about 2.5 to about 5.0, a is from about 0.95 to about 1.25, and b is from  
4 about 0.02 to about 0.10.
- 1 13. The thin film composite of Claim 6, wherein the barrier layer is incorporated as  
2 depicted in either Figures 1(b), 1(c), or 1(d).

1 14. The thin film composite of Claim 6, wherein the metallic foil substrate is a  
2 textured substrate with an enhanced surface area as depicted in either Figures 1(e) or 1(f).

1 15. The thin film composite of Claim 6, further comprising a parallel interconnection  
2 of dielectric metallic foil systems, or a series interconnection of dielectric metallic foil  
3 systems, as depicted in either Figures 1(g) or 1(h), respectively.

1/8

Fig. 1(a)

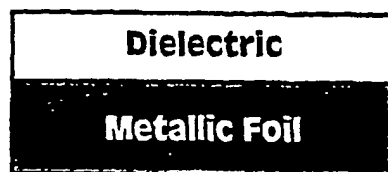


Fig. 1(b)

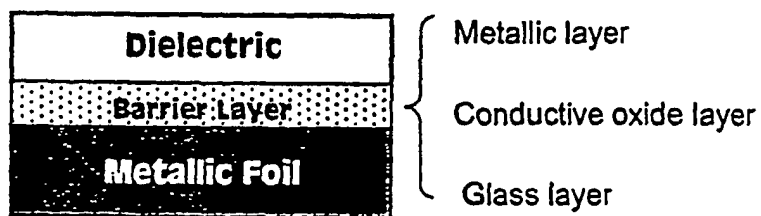


Fig. 1(c)

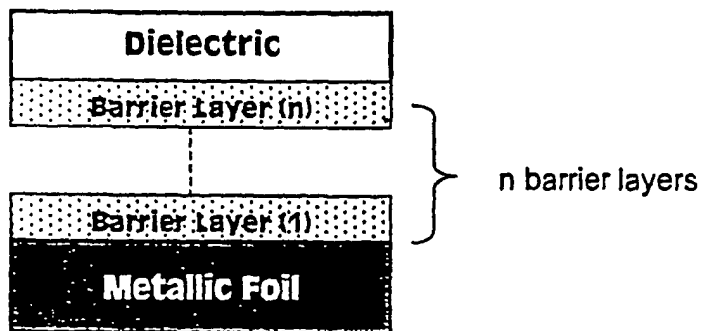


Fig. 1(d)

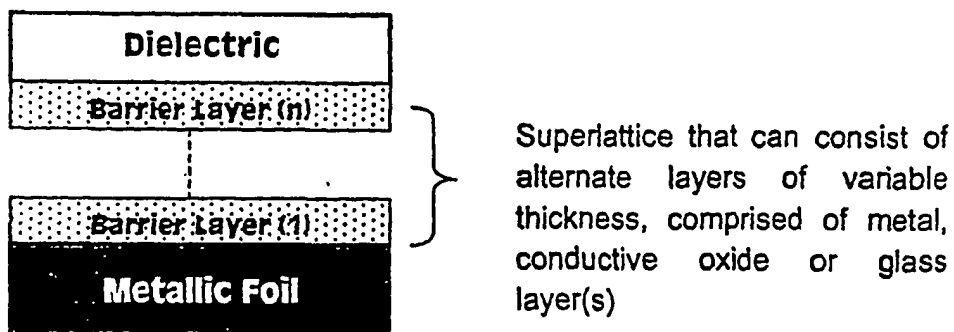




Fig. 1 (e)

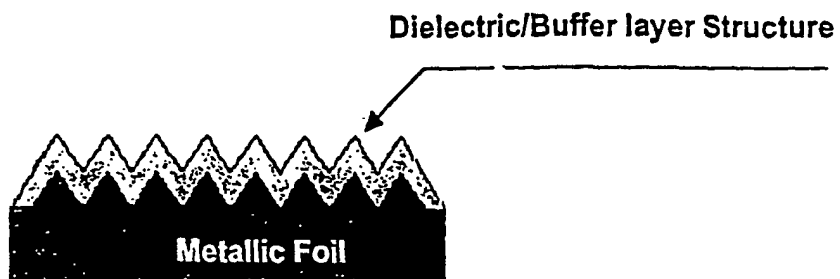


Fig. 1 (f)

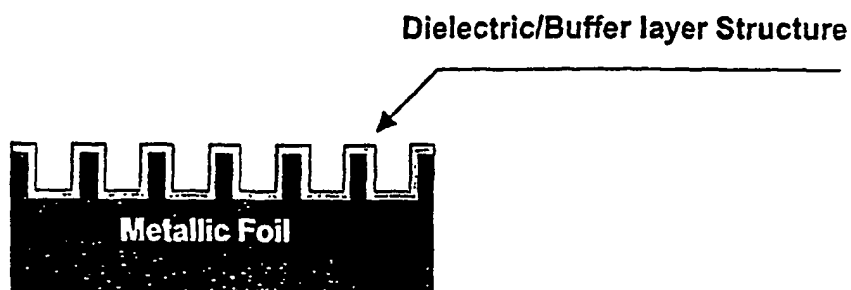


Fig. 1(g)

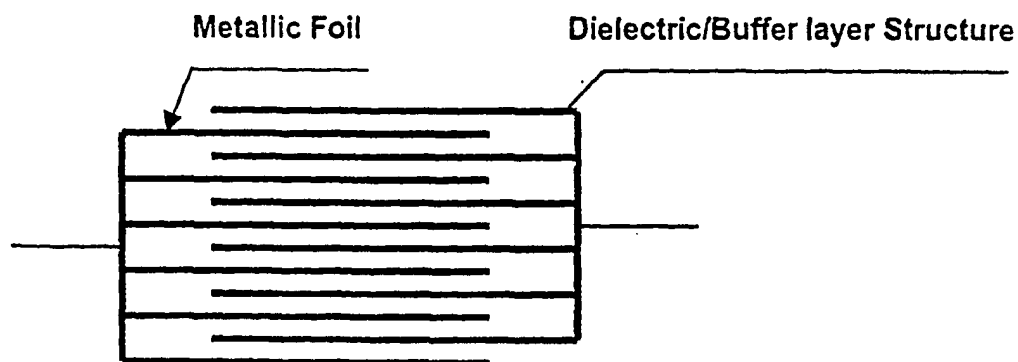
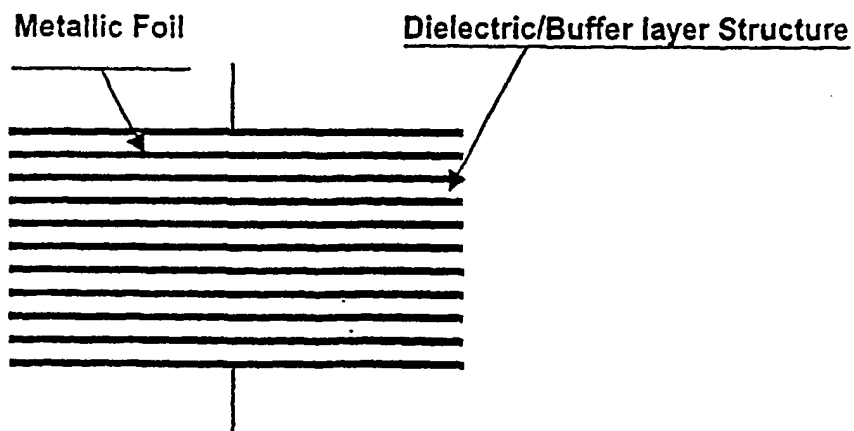


Fig.1(h)



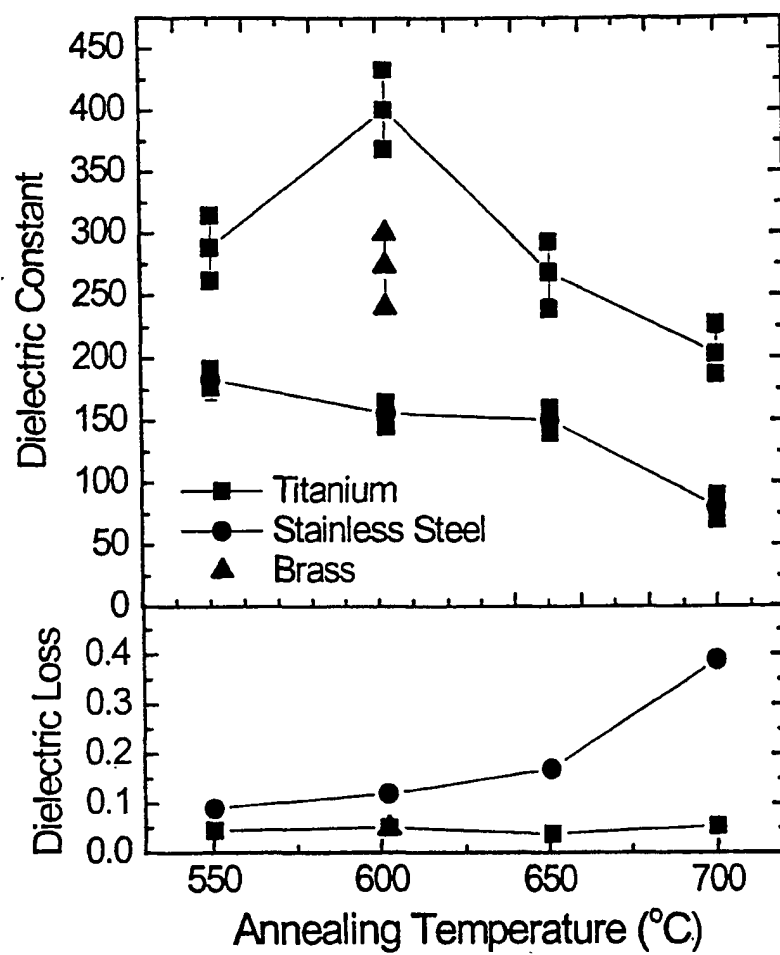


Fig.2

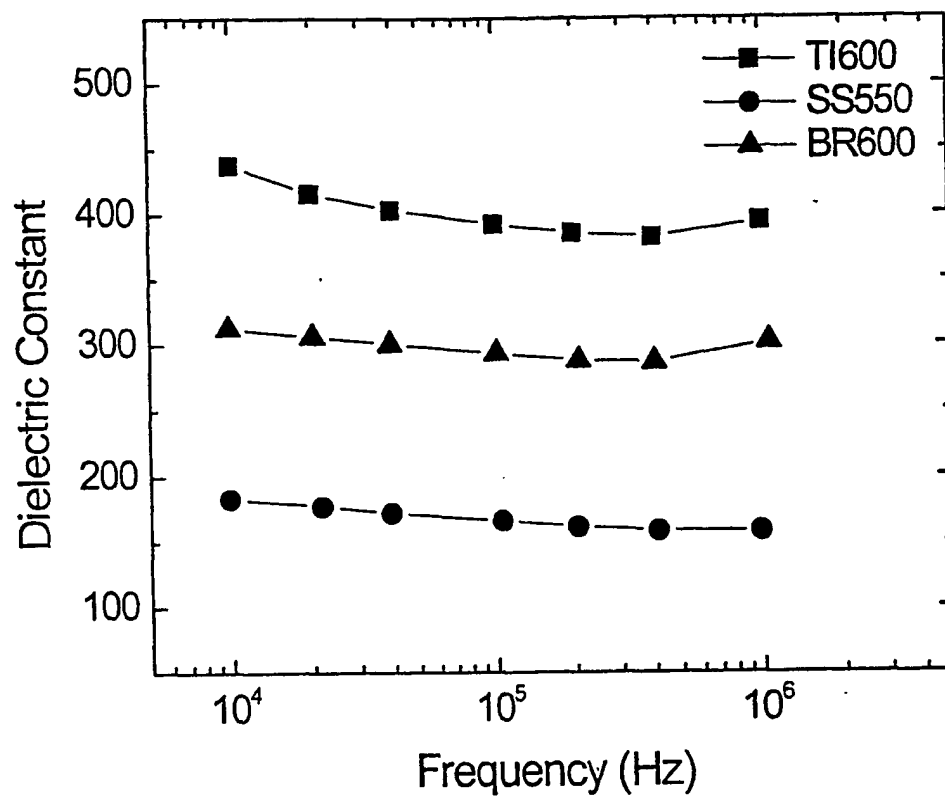


Fig. 3

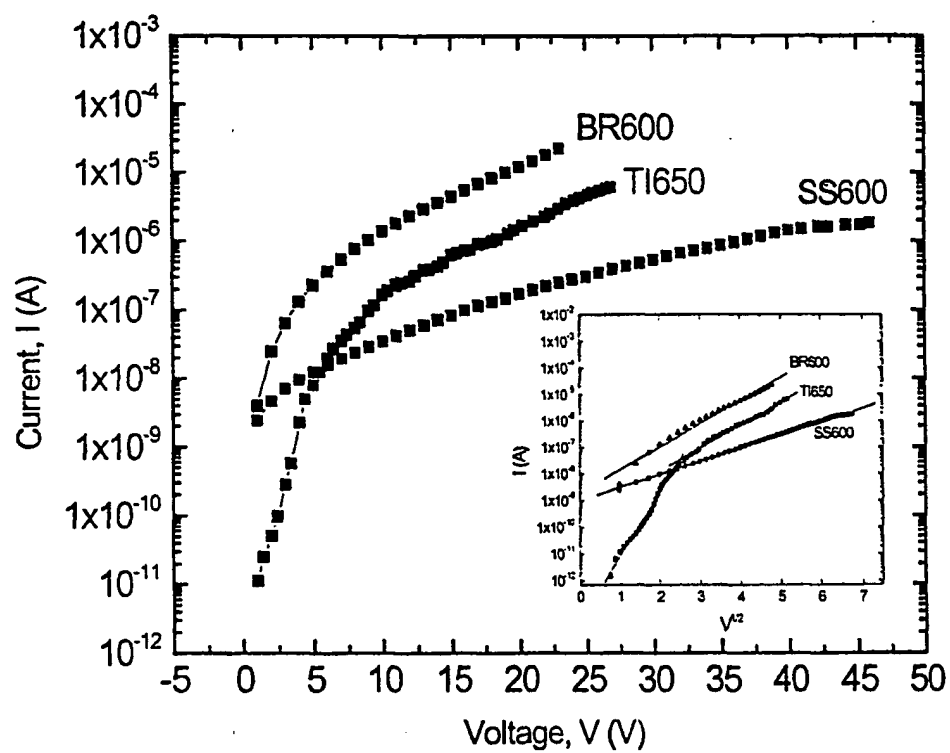


Fig.4

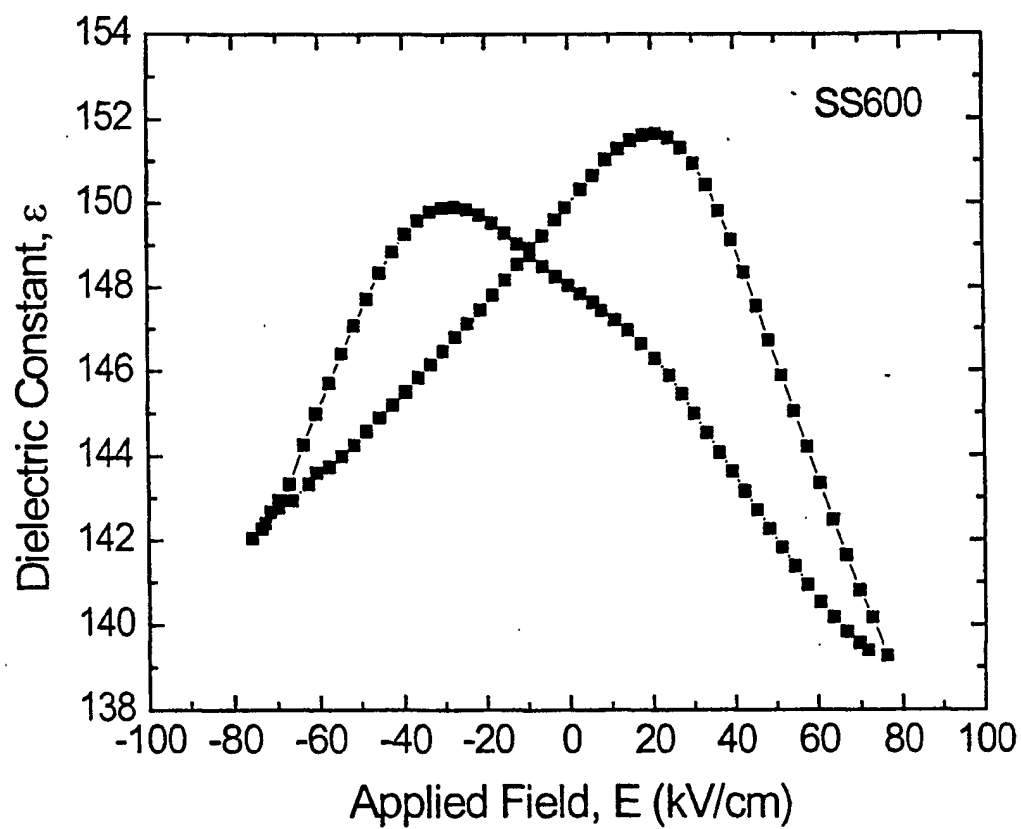


Fig.5 (a)

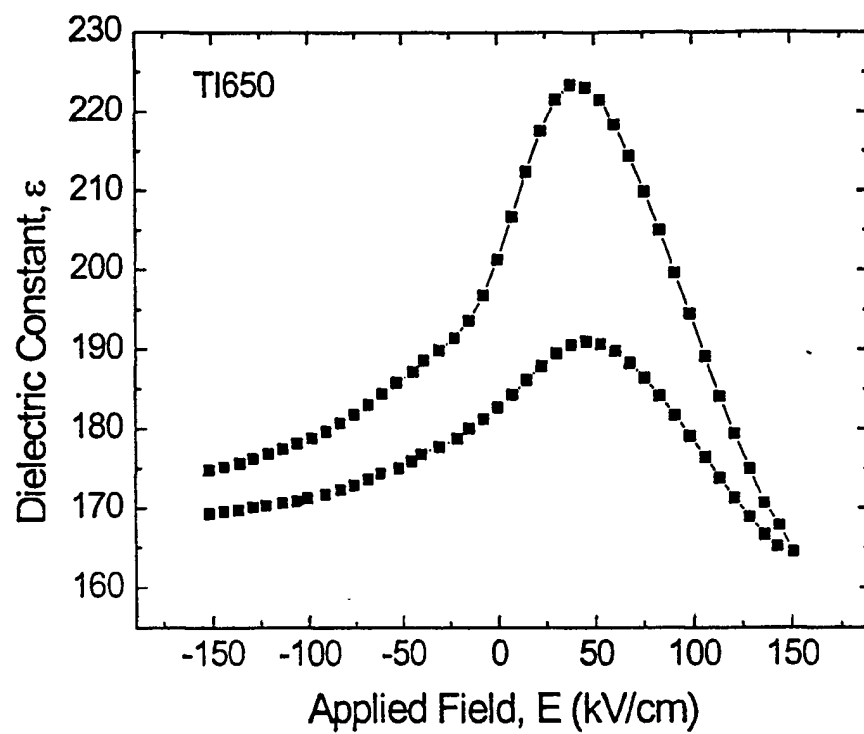


Fig.5 (b)

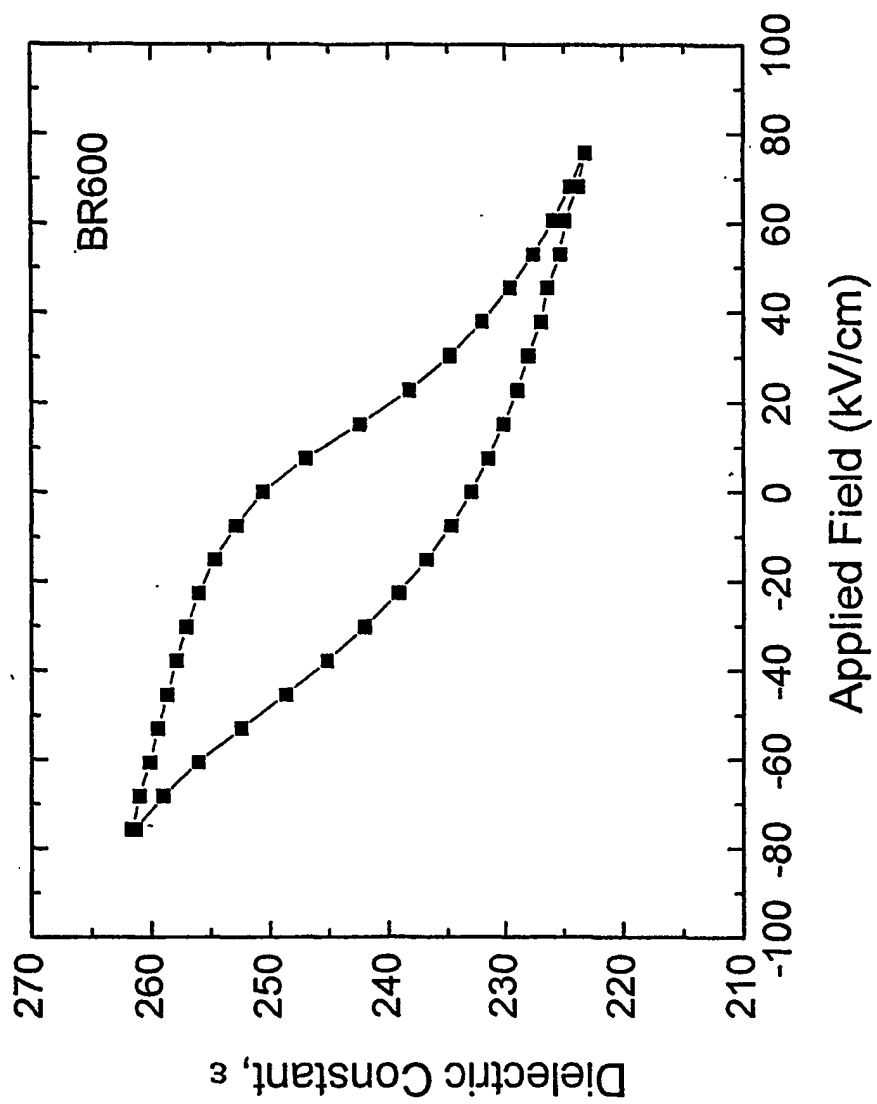


Fig.5 (c)

(19) World Intellectual Property Organization  
International Bureau



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

(43) International Publication Date  
13 September 2001 (13.09.2001)

PCT

(10) International Publication Number  
WO 01/67465 A3

(51) International Patent Classification<sup>7</sup>: H01G 4/12

(21) International Application Number: PCT/IB01/00290

(22) International Filing Date: 1 March 2001 (01.03.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
09/518,532 4 March 2000 (04.03.2000) US

(71) Applicant: ENERGENIUS, INC. [CA/CA]: 840 York Mills Road, North York, Ontario M3B 3A8 (CA).

(72) Inventors: ZOU, Qin; 260 Wellesley Street East, Apt. 2218, Toronto, Ontario M4X 1G6 (CA). YACOBI, Ben,

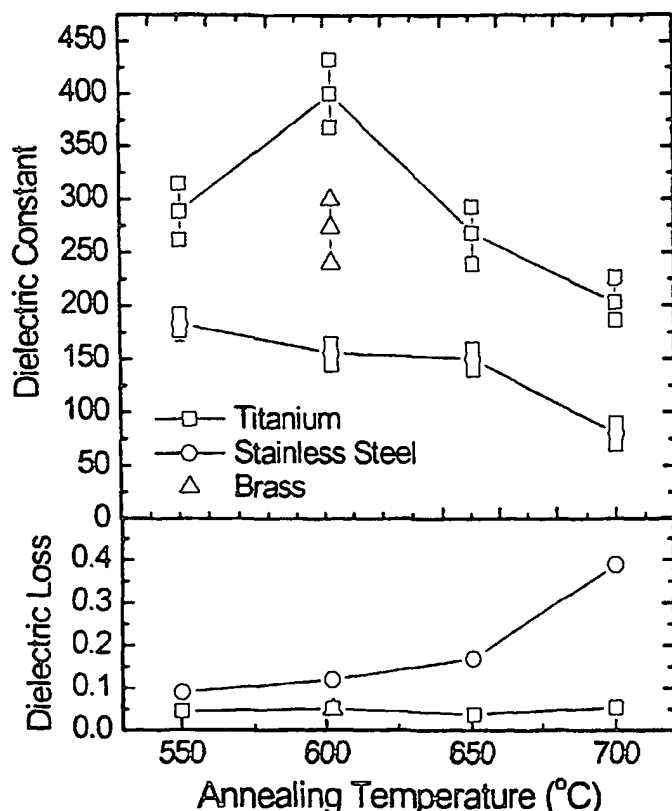
G.: 1700 The Collegeway, #405, Mississauga, Ontario L5L 4M2 (CA). RUDA, Harry, Eugen: 21 Brookfield Road, North York, Ontario M2P 1B1 (CA). FARRELL, Mark: RR#4, P.O. Box 687, Georgetown, Ontario L9Y 4E8 (CA).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW). Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM). European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR). OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: LEAD ZIRCONATE TITANATE DIELECTRIC THIN FILM COMPOSITES ON METALLIC FOILS



(57) Abstract: Crystalline dielectric lead zirconate titanate thin film composites on metallic foils exhibit high dielectric constants, low dielectric loss (loss tangent of less than 5 %) and low leakage current. The lead zirconate titanates may be of the formula  $PbZr_xTi_yO_2$  (PZT) herein x and y are independently from about 0.35 to about 0.65 and z is from about 2.5 to about 5.0. The thin foil dielectric composites can be prepared by a variety of methods including deposition of PZT thin films on brass, platinum, titanium and stainless steel foils using sol-gel processing, sputtering deposition and chemical vapor deposition.

WO 01/67465 A3





**Published:**

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**(88) Date of publication of the international search report:**  
28 February 2002

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 01/00290

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01G4/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01G H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 513 478 A (MITSUBISHI MATERIALS CORPORATION) 19 November 1992 (1992-11-19) page 2, line 36 - line 43 page 3, line 3 - line 7 ---	1-4
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 01 & JP 10 270766 A (OSAKA GAS CO LTD), 9 October 1998 (1998-10-09) abstract ---	1-3, 6, 13
A	EP 0 441 408 A (MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.) 14 August 1991 (1991-08-14) claim 1 -----	7-12

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

19 October 2001

Date of mailing of the international search report

26/10/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Goossens, A

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 01/00290

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 513478	A	19-11-1992	JP 4259380 A	14-09-1992
			DE 69226898 D1	15-10-1998
			DE 69226898 T2	04-03-1999
			EP 0513478 A2	19-11-1992
			JP 3021930 B2	15-03-2000
			JP 6116095 A	26-04-1994
			KR 9706997 B1	01-05-1997
			US 5453294 A	26-09-1995
<hr/>				
JP 10270766	A	09-10-1998	NONE	
<hr/>				
EP 441408	A	14-08-1991	JP 2532381 B2	11-09-1996
			JP 62205266 A	09-09-1987
			EP 0441408 A2	14-08-1991
			DE 3752094 D1	21-08-1997
			DE 3752094 T2	12-02-1998
			DE 3789909 D1	07-07-1994
			DE 3789909 T2	05-01-1995
			EP 0237250 A1	16-09-1987
			US 5308462 A	03-05-1994
<hr/>				